OFFICE OF NAVAL RESEARCH

FINAL REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-92-J-1415

R&T Code: 400x099yip01

"High Temperature Polymers for Second Order Nonlinear Optics: Photorefractive Polyimides for Photonic Materials"

Principal Investigator: Hilary S. Lackritz
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West Lafayette, Indiana 47907-1283

May 12, 1995

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Contract/Grant Number: N00014-92-J-1415
Contract/Grant Title: High Temperature Polymers for Second Order Nonlinear Optics: Photorefractive Polyimides for Photonic Materials
Principal Investigator: Hilary S. Lackritz
Mailing Address: School of Chemical Engineering, 1283 CHME Building Room 7B, Purdue University, West Lafayette, Indiana 47907-1283

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E-mail Address: lackritz@ecn.purdue.edu

a. Number of papers submitted to refereed journals, but not published: 7

Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. "Dopant Orientation Dynamics in Doped Second Order Nonlinear Optical Amorphous Polymers. 3. Effect of Hydrogen Bonding" *J. Polym. Sci., Polym. Phys.*, in press.

Wright, M. E.; Toplikar, E. G.; Lackritz, H. S.; Subramanyan, S. "A Preliminary Study of Poly(p-phenylene) Based NLO Materials" *Makromol. Chemie,* in press.

Subramanyan, S.; Liu, L.Y.; Lackritz, H.S.; Wright, M. E.; McFarland, I.; Petteys, B. J. "Relaxations in Indole-Based Polymers and the Synthesis of Stabilized Polymer Blends and Main-Chain and Side-Chain Functionalized Polymers for Second Order Nonlinear Optics" *Chem. Mater.*, in review.

Ghebremichael, F.; Lackritz, H.S. "Linear Electro-Optic Effects of Dye-Doped Polymers: Termperature and Poling Field Dependencies" *J. Appl. Phys.*, submitted 1/95.

Fu, C.Y.S.; Lackritz, H.S.; Priddy, D. B. Jr.; McGrath, J.E. "Polymer Physics and Structure/Property Relationships of Thermally Stable Polyarylene Ethers for Second Order Nonlinear Optics" *Macromolecules*, submitted 1/95.

Chen, F.; Subramanyan, S.; Lackritz, H.S. "Photopolymerization Dynamics of Acrolein onto Metal Substrates Using Surface Second Harmonic Generation" *Materials Research Society Symposium Series,* **1995**, in press.

Sullivan, L. A.; Lackritz, H. S. "Dynamic Mechanical Analysis and Dielectric Relaxation for Second Order Nonlinear Optical Applications" *Materials Research Society Symposium Series,* **1995**, in press.

b. * Number of papers published in refereed journals: 7

Wright, M. E.; Mullick, S.; Lackritz, H. S.; Liu, L.-Y. "Organic NLO Polymers. 2. A Study of Main Chain and Guest-Host $\chi^{(2)}$ NLO Polymers: NLO-phore Structure Versus Poling" *Macromolecules*, **1994**, *27*, 3009.

Wright, M.E.; Toplikar, E.G.; Lackritz, H.S.; Kerney, J.T. "Organometallic NLO Polymers 4. Organometallic Main-Chain, Side-Chain, and Guest-Host Polymers: A Study of Their Orientation and Relaxation Using Second Harmonic Generation" *Macromolecules,* **1994**, *27*, 3016.

Liu, L. Y.; Ramkrishna, D.; Lackritz, H. S. "Rotational Brownian Motion of Chromophores and Electric Field Effects in Polymer Films for Second Order Nonlinear Optics" *Macromolecules,* **1994**, *27*, 5987.

Lackritz, H.S.; Liu, L.-Y.;Wright, M.E.; Mullick, S. "Study of Poling and Relaxation in Kink and Linear Main-Chain Functionalized Polymers for Second Order Nonlinear Optical Applications" *Macromolecules,* **1995**, *28*, 1912.

Pasmore, T.; Talbot, J.; Lackritz, H. S. "Monte-Carlo Simulations of Electric Field Hopping in Doped Polymer Thin Films" *Nonlinear Optics*, in press, to appear in May, 1995.

Fu, C.-Y. S.; Lackritz, H. S.; Priddy, D. B.; McGrath, J. E. "Synthesis and Characterization of High Temperature Stable Polymers for Second Order Nonlinear Optical Applications" *Materials Research Society Symposium Series,* **1994**,*328*, 589.

Priddy, D. B.; Fu, C.-Y. S.; Lackritz, H. S.; McGrath, J. E. "Phosphorus Containing Poly(arylene ether)s as Second Order Nonlinear Optical Materials" *Materials Research Society Symposium Series,* **1994**,*328*, 547.

Haber, K. S.; Ostrowski, M. H.; Lackritz, H. S. "Characterizing the Distribution of Space Charge in Poled Polymer Films" *Materials Research Society Symposium Series,* **1994**,*328*, 595.

c. Number of books or chapters submitted, but not yet published: 1

Fu, C.S.Y.; Ostrowski, M.H.; Lackritz, H.S. "Dielectric Relaxation Studies of Polymeric Nonlinear Optical Materials" in Dielectric Spectroscopy of Polymeric Materials, Runt, J. P. and Fitzgerald, J. J., Eds. ACS Symposium Series #XXX, American Chemical Society, Washington, D.C., in review. (*Invited Publication*)

d. * Number of books or chapters published: 1

Wright, M. E.; Toplikar, E. G.; Lackritz, H. S.; Kerney, J. T. "New Organometallic Polymeric Materials: The Search for Organometallic NLO Polymers" in *Inorganic and Organometallic Polymers*, Alcock, H., Wynne, K., and Wisian-Neilson, P., Eds., ACS Symposium Series #XXX, American Chemical Society, Washington, D.C. **1995**, in press.

e. * Number of printed technical reports/non-refereed papers: 6

Wright, M. E.; McFarland, I.; Pettys, B. J.; Lackritz, H. S.; Liu, L. Y. "Organic NLO Polymers. 5. Homopolymerization of Indole Based NLO-phore: A Heterocycle $\chi^{(2)}$ Main-Chain Polymer" *Polymer Preprints*, **1994**, *35 (1)*, 470.

Lackritz, H. S.; Ostrowski, M. H.; Liu, L.-Y.; Fu, C.Y. S.; "Dielectric Relaxation and Electric Field Effects in Polymers For Second Order Nonlinear Applications" *Polym. Mater. Sci. Eng. Preprints,* **1994**, *70*, 392.

Subramanyan, S.; Chen, F.; Lackritz, H. S. "Nonlinear Optical Studies of Photopolymerization at the Metal Interface" *Polymer Preprints*, **1994**,*35(2)*, 277.

Lackritz, H. S.; Liu, L.-Y. "Polymer Relaxations in Polymers for Second Order Nonlinear Optical Applications" *Polymer Preprints*, **1994**, *35(2)*, 202.

Wright, M. E.; McFarland, I.; Lackritz, H. S.; Subramanyan, S.; Liu, L. Y. "A Novel Approach for the Synthesis of Side-Chain, IPN, and Cross-linked Nonlinear Optical Polymers" *Polymer Preprints*, **1994**, *35(2)*, 126.

Fu, C.Y.-S; Priddy, D. B.; McGrath, J. E.; Lackritz, H. S. "Polymer Physics for Second-Order Nonlinear Optics" *Proc. Soc. Photo-Opt. Instrum. Eng.*, **1994**, *2258*, 153.

f. Number of patents filed: 0
g. * Number of patents granted: 0
h. * Number of invited presentations: 10

*Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the University of Michigan, Department of Materials Science, Ann Arbor, MI, April 1994.

Fu, C.Y.-S; *Lackritz, H. S. "Polymer Relaxations in Doped and Functionalized Systems Studied Using Second Order Nonlinear Optics" presented at the Society for Photo-optic Instrumentation Engineers meeting in San Diego, CA, July 1994.

Sullivan, L.; Ostrowski, M.; *Lackritz, H. S.; "Polymer Physics in Poled Polymers Studied Using Second Order Nonlinear Optics, Dielectric Relaxation, and Dynamic Mechanical Analysis" presented at Wright-Patterson Air Force Base in Dayton, OH, August 1994.

*Lackritz, H. S.; Liu, L.-Y. "Polymer Relaxations in Doped and Functionalized Systems Studied Using Second Order Nonlinear Optics" presented at the American Chemical Society/Optical Society of American meeting in Washington, DC, August 1994.

*Lackritz, H. S. "Polymer Physics and Electric Field Effects in Poled Polymers for Second Order Nonlinear Optical Applications" presented at Cornell University, Department of Chemical Engineering, Ithaca, NY, September, 1994.

*Lackritz, H. S. "Processing of Polymers for Second Order Nonlinear Optics" presented at the Engineering Research Center, University of Wisconsin, Madison, WI, October 1994.

*Lackritz, H. S. "Design and Development of Polymers for Second Order Nonlinear Optics" presented at Utah State University, Department of Chemistry, Logan, UT, December 1994.

*Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the University of Nebraska, Department of Mechanical and Materials Engineering, Lincoln, NE, February 1995.

Sullivan, L.; *Lackritz, H. S. "Characteristic Relaxation Times in Polymers Studied by Nonlinear Optics, Dielectric Relaxation, and Dynamic Mechanical Analysis" presented at Wright-Patterson Air Force Base in Dayton, OH, April, 1995.

*Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the Massachusetts Institute of Technology, Polymer Seminar Series, Cambridge, MA, May 1995.

i. * Number of submitted presentations: 10

*Subramanyan, S.; Chen, F.; Lackritz, H. S. "Nonlinear Optical Studies of Photopolymerization at the Metal Interface" presented at the American Chemical Society/Optical Society of American national meeting in Washington, DC, August 1994.

*Fu, C.Y.S.; Lackritz, H. S.; Priddy, D. B.; McGrath, J. E. "Second Harmonic Generation and Dielectric Relaxation Studies of High Temperature Nonlinear Optical Polymers" presented at the American Institute of Chemical Engineers national meeting in San Francisco, CA, November 1994.

*Liu, L.-Y.; Ramkrishna, D.; Lackritz, H. S. "The Rotational Brownian Motion of Chromophores and Electric Field Effects in Polymer Films for Second Order Nonlinear Optics" presented at the American Institute of Chemical Engineers national meeting in San Francisco, CA, November 1994.

*Ostrowski, M.; Haber, K.; Lackritz, H. S. "Electric Field Effects in Polymer Thin Films Studied Using Electrochromism, Dielectric Relaxation and Second Order Nonlinear Optics" poster presented at the American Physical Society national meeting in San Jose, CA, March 1995.

*Ghebremichael, F.; Lackritz, H. S. "Electro-optic and Second Harmonic Generation Studies of Dye-Doped Thin Film Polymers" presented at the American Physical Society national meeting in San Jose, CA, March 1995.

*Subramanyan, S.; Chen, F.; Lackritz, H.S. "Kinetic Studies of Photopolymerization at Metal Surfaces Using Surface Second Harmonic Generation" poster presented at the American Physical Society national meeting in San Jose, CA, March 1995.

*Pasmore, T. A.; Talbot, J.; Lackritz, H. S. "Charge Transport through Chromophore Doped Polymer Thin Films for Second Order Nonlinear Optics" poster presented at the American Physical Society national meeting in San Jose, CA, March 1995.

*Sullivan, L. A.; Lackritz, H. S. "Dynamic Mechanical Analysis and Dielectric Relaxation for Electro-Optical Polymer Applications" presented at the Materials Research Society national meeting in San Francisco, CA, April 1995.

*Chen, F.; Subrahmanyan, S.; Lackritz, H. S. "Gas Phase Photopolymerization of Vinyl Monomers on Metallic Substrates Studied Using Surface Second Harmonic

Generation" presented at the Materials Research Society national meeting in San Francisco, CA, April 1995.

*Lackritz, H. S. "Electric Field Effects in Polymer Thin Films" to be presented at the International Conference on Organic Nonlinear Optics in Gunma, Japan, July 1995.

j. * Honors/Awards/Prizes for contract/grant employees:
Presidential Faculty Fellows Award (National Science Foundation) 1993-1998
Office of Naval Research Young Investigator Award 1992-1995
Shreve Award for Outstanding Undergraduate Teaching, Second Place, Chemical Eng., 1994; Shreve Award for Outstanding Undergraduate Teaching, Second Place, Chemical Eng., 1995

American Chemical Society/Optical Society of America (ACS/OSA) Symposium on Thin Films for Photonic Applications
International Advisory Committee 1994-
ACS Program Organizer and Chair 1995 Portland Optical Society of America meeting
Symposium Organizer 1998 Orlando American Chemical Society meeting

American Physical Society (Division of High Polymer Physics APS DHPP) Publications Committee (1993-) Publication Committee Chair, 1996
Guest Editor: Journal of Polymer Science: Polymer Physics 1996 APS DHPP Special Issue

Session Chair - "Dielectric Relaxation in Polymeric Systems," American Chemical Society Meeting, March 1994, San Diego, CA.
Session Chair- "Electrically and Optically Active Polymers II," American Physical Society Meeting, March 1995, San Jose, CA.
Session Chair and Organizer- "Polymers for Optoelectronics and Photonics," American Institute of Chemical Engineers Meeting, November 1994, San Francisco, CA.

k. Total number of **Full-time equivalent** Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:
Graduate Students: 2
Post-Doctoral Associates: 0
including the number of,
Female Graduate Students: 1
Female Post-Doctoral Associates: 0
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0
Of the 8 graduate students in my group, 3 are female, and of the three post-doctoral associates, 2 are female and the other is minority.

l. * Other funding see attached.

Hilary S. Lackritz

SUPPORTING AGENCY AND PROJECT NUMBER	TOTAL $ AMOUNT	EFFECTIVE AND EXPIRATION DATE	% OF TIME COMMITTED	TITLE OF PROJECT
Current:				
NSF/PFF	$500,000	9/1/93-8/31/98	2.5 mo. SS	Novel Optical Techniques for Studying Polymer-Metal Interfaces: Surface Second Harmonic Generation
AFOSR	$317,246	5/1/93-4/31/96	5% AY	Nonlinear Optical and Charge Distribution Studies Probing Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optics
NSF	$168,300	1/15/93-1/14/96	5% AY	Charge Distribution and Nonlinear Optical Studies Probing Electric Field Effects in Polymer Thin Films
ONR Young Investigator	$285,000	4/1/92-6/1/95	5% AY	High Temperature Polymers for Second Order Nonlinear Optics: Photorefractive Polyimides for Photonic Materials
ONR/AASERT	$90,000	6/1/93-5/31/96		High Temperature Stable Polymers for Second Order Nonlinear Optics
NSF/EQUIP	$77,533	10/1/93-9/30/95		Spectroellipsometer Equipment for Determining Optical Properties, Thickness and Orientation of Polymeric Materials (joint with E.I. Franses)
Lockheed Missiles and Space Company	$25,000	2/1/95-1/31/96		Electro-optic Polymer Development Contract (subcontract through Wright Patterson Air Force Base- funded Proposal)
Exxon Education Foundation	$30,000	10/31/91-10/1/95		Minority Student Education Program
NSF/REU	$150,000	5/1/93-4/30/96		An REU Site in Chemical Engineering (joint with E.I. Franses, J. M. Wiest, N. A. Peppas, J.M. Caruthers, W.N. Delgass, and J.F. Pekny)
NFS/MPS/ ENGR/EHR	$350,000	8/17/92-8/16/95	4% AY .5 mo SS	An Innovative Undergraduate Materials Curriculum (joint with D.R. Gaskell J.M. Caruthers, K.P. Trumble, K.J. Bowman, and N.A. Peppas).
NSF/Equip	$350,100	8/1/94-7/31/95		Infrared-Visible Sum Frequency Generation as a Spectroscopic Probe of Chemical Structure and Dynamics at Interfaces (joint with T. S. Zweir, C. Johnston, D. Ben-Amotz, C. P. Kubiak, E. R. Grant, and M. Weaver)
ONR	$180,949	6/1/95-5/31/97		Structure/Property Relationships and Polymer Physics in High Temperature Stable Polymers for Second Order Nonlinear Optics
AFOSR/AASERT	$90,000	6/1/95-5/31/98		Characterization of Optical Properties of Thin Nonlinear Optical Polymer Films for Device Applications as a Function of Processing
Pending:				
Exxon Education Foundation	$15,000	10/31/95-10/1/96		Minority Student Education Program-continuation

PART II: SUMMARY OF PROGRESS

a) PI: Professor Hilary S. Lackritz
b) Phone: (317) 494-4065; (317) 494-0805 fax; e-mail: lackritz@ecn.purdue.edu
c) ONR Scientific Officer: Dr. Kenneth J. Wynne, Chemistry Division

d) DESCRIPTION OF PROJECT

We are examining a variety of novel high temperature stable polymers as new materials for second order nonlinear optical (NLO) device applications and modelling the rotational Brownian dynamics of chromophore orientation. Current polymers have sufficient optical signal generated by available chromophores, but are not practical for devices because of limitations in the temporal and thermal stability of the active chromophore orientation in the polymer matrix. This experimental and theoretical approach for developing a new class of photonic materials with superior thermal and temporal stability is a first attempt to design second order NLO polymer with controllable, tailorable local physical and electrical properties. A second, equally important goal is to theoretically and experimentally understand the basic polymer physics controlling the thermal and temporal stability of the optical chromophore orientation. This will determine not only the overall efficiency of the materials for device applications, but will generate substantial information about local mobility in high temperature stable polymers.

e) SIGNIFICANT RESULTS 5/1/94-4/31/95

This work is the first comprehensive experimental and theoretical study probing the orientational and relaxation behavior of guest-host, side chain and main chain functionalized (linear and kinked) polymer systems and polymer blends including indoles, p-polyphenylenes, and other high temperature stable systems as a function of polymer processing. Dipolar main-chain NLOP's show a strong resistance to alignment; thus, a more rigid polymer backbone is in itself not a solution to high temperature stable NLO materials. Hydrogen bonding sites rigidly connected to the NLO-phore improve temporal stability and do not harm the alignment.

f) PLANS FOR THE FOLLOWING YEAR

Several guest-host, side-chain, and main-chain functionalized polymers synthesized by Prof. Michael Wright (Utah State) including a series of polyphenylenes, indoles, and others have been and will continue to be examined as materials for high temperature stable second order NLO materials. We will also characterize his "molecular chandelier" molecules (work funded by ONR). Nonlinear optics (including second harmonic generation and electro-optic measurements), differential scanning calorimetry, infrared, dielectric, and dynamic mechanical spectroscopies have been used in concert in order to maximize studies of the thermal and temporal stability of chromophore orientation following poling. NMR experiments, performed by Dr. Larry Merwin at China Lake, will allow us to further understand the polymer dynamis. We will continue to develop processing methodologies for the successful high temperature stable PEPO polymers synthesized by Prof. McGrath at VPI, showing enhanced stability caused by hydrogen bonding between the chromophore and polymer and by the increased stiffness of the backbone. With assistance from collaborators at Akzo-Nobel Electronic Products and Lockheed Missiles and Space Company, materials will be tested in device configuration.

g) Graduate Students Funded in Year 2: Ms. Leah Sullivan and Mr. Daniel Randall.

Part III.
a. Introductory view-graph discussing research
b. Figure representing the highlight
c. Concluding view-graph
d. Paragraph of explanatory text

In order for the nonlinear optical polymers to be practical for military applications, long-term optical stability at operating temperatures as high as 80-125°C and at processing temperatures that may exceed 250°C, is required. Our research focuses on developing polymers with high Tg's and rigid backbones that yield long-term thermal and temporal stability. Currently these systems, synthesized by Michael Wright at Utah State and Jim McGrath at VPI, include poly(*p*-phenylene)s, poly(arylene ether) phosphine oxides, and indole guest-host, side-chain, and main-chain functionalized systems. Indole-based polymer blends synthesized using novel techniques are also developed. The goal of our research is to study polymer physics including structure/property relationships; in particular, the dopant/polymer interactions, chromophore functionalization, and polymer backbone structures that affect the chromophore orientational dynamics in polymer systems. Understanding the polymer physics of these systems will allow us to better tailor materials for nonlinear optical device applications. In addition, the principles learned here will have an impact on many aspects of general novel materials design and development.

HIGH TEMPERATURE STABLE POLYMERS FOR SECOND ORDER NONLINEAR OPTICAL APPLICATIONS

Hilary S. Lackritz,
Chemical Engineering, Purdue University
ONR YIP, Chemistry Division;
Dr. Ronald DeMarco, Director
Dr. Kenneth J. Wynne, ONR Scientific Officer

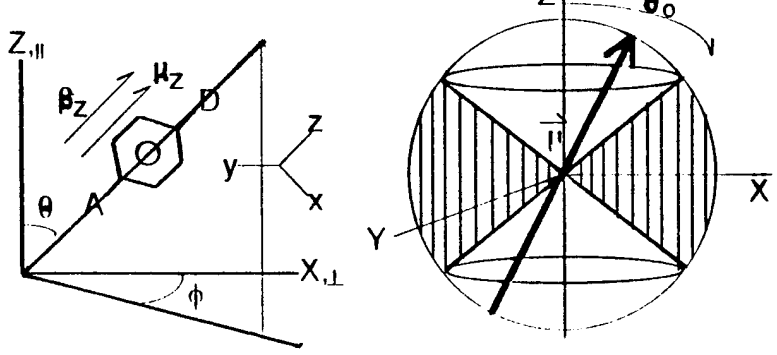
High Temperature Stable Polymers Investigated:

- poly(arylene ether) phosphine oxides
- poly(*p*-phenylenes)
- indole main-chain, side-chain, guest-host
- indole-based polymer blends

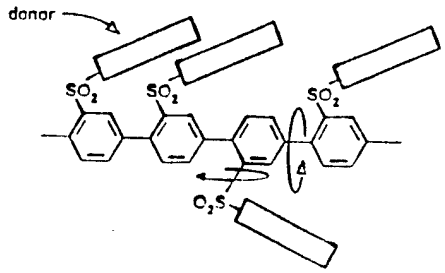
collaborators: Michael Wright, Utah State and James McGrath, VPI (ONR grantees)

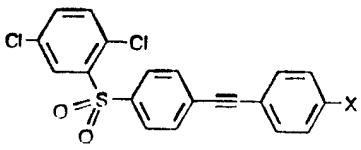
Examined rotational Brownian motion of chromophores and local electric field effects in polymer systems in order to quantify thermal and temporal stability characteristics and eventually to predict independently the stability of the NLO materials.

Probability Density of finding molecule at θ at time t; p = p(θ, t).

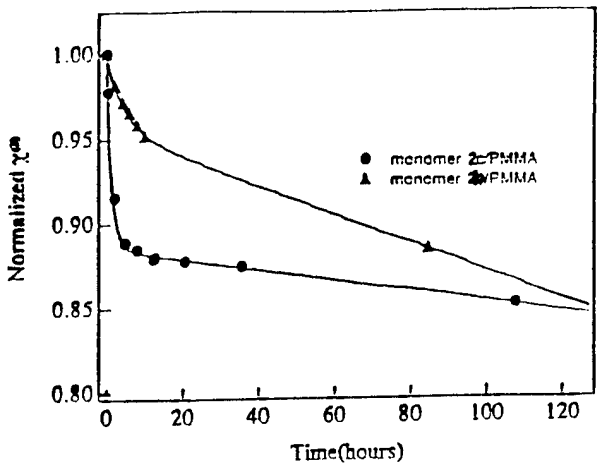


Poly(p-phenylene)-based NLO Materials

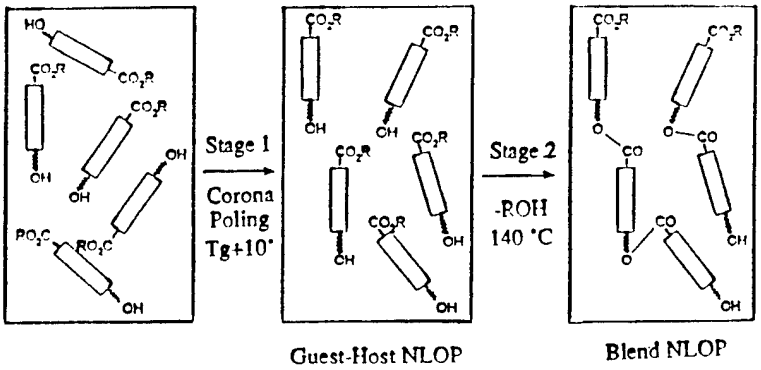


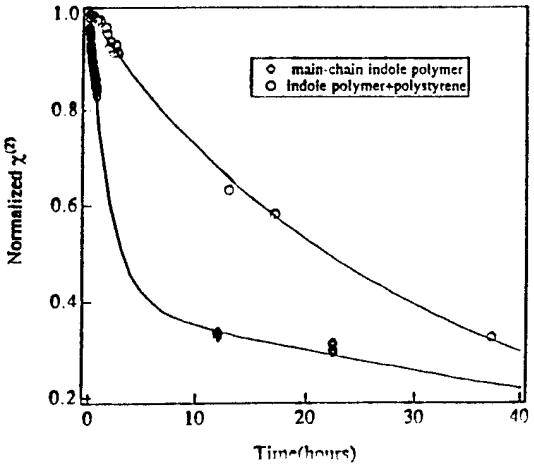


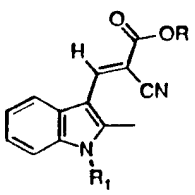
	$\chi^{(2)}$ pm/V
2b, X= OMe	0.9
2c, X= NMe_2	1.7



Indole-based NLO polymers







2b, $R_1 = (CH_2)_6OH$

9, $R_1 = CH_3$

Polystyrene (PS) host

T_g = 105

M_n = 250,000

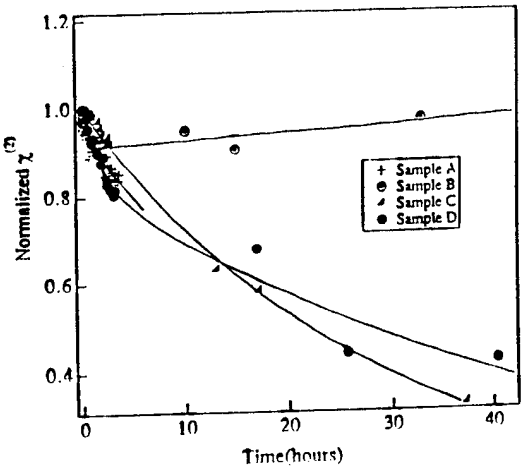
Sample A, 10 wt-% NLO-phore 9, no catalyst

Sample B, 10 wt-% NLO-phore 9, Sn(IV) catalyst

Sample C, 10 wt-% NLO-phore 2b, no catalyst

Sample D, 10 wt-% NLO-phore 2b, Sn(IV) catalyst

140 deg C



Conclusions

Technological Advances:

Stable for longer times at higher temperatures
Retards chromophore disorientation following poling
Easy to Process
Tailorable

Characterize thermal and temporal stability of poled polymers for second order nonlinear optical applications, including electro-optic and photorefractive devices;

To improve tailorability, critical to understand basic polymer physics and structure/property relationships governing chromophore orientational dynamics in high temperature stable systems

Second order NLO and a variety of other experimental techniques including dielectric relaxation and dynamic mechanical analysis used to examine specific issues including how

dopant/polymer interactions
polymer backbone structure
chromophore functionalization

influence chromophore orientational dynamics as a function of processing.

Novel theoretical treatments promise predictive results.

PART II: SUMMARY OF PROGRESS: AASERT GRANT No. N00014-93-1-0903

a) PI: Professor Hilary S. Lackritz
b) Phone: (317) 494-4065; (317) 494-0805 fax; e-mail: lackritz@ecn.purdue.edu
c) ONR Scientific Officer: Dr. Angela Erwin, Code 1113PO, Chemistry Division

d) Description of Progress

In order for NLO polymers to be practical for military applications, long-term optical stability at operating temperatures as high as 80-125°C and at processing temperatures that exceed 250°C is required. Recent research focuses on synthesizing polymers with high Tg's and rigid backbones that yield long-term stability. The polymer physics behind how these matrices prevent the randomization of chromophore orientation following poling, improving the optical stability, is poorly studied. The primary objective of this research is to investigate polymer physics including structure/property relationships; in particular, the dopant/polymer interactions, chromophore functionalization, physical aging, molecular weight, and polymer backbone structures that affect the relaxation behavior of these systems. Gaining knowledge on how these polymers behave will enable predictions of long-term thermal properties throughout the anticipated service life when utilizing them for engineering applications.

e) SIGNIFICANT RESULTS

Systematic studies on how structure/property relationships influence the chromophore orientational dynamics and polymer relaxations in the thermally stable NLO polyarylene ethers (synthesized by Prof. J. McGrath at VPI) have been performed. By combining second harmonic generation and dielectric relaxation, specific issues such as the effects of polymer backbone structures and molecular weight, dopant/polymer interactions, chromophore functionalization, and chromophore concentration on the segmental relaxation behavior and intermolecular cooperativity in these polymeric systems have been investigated. Attempts to correlate the molecular level parameters including the molecular weight and polydispersities to the observed physical properties were made. The effect of physical aging during poling on the temporal stability of chromophore orientation was also studied. This information is critical in order to better tailor the materials for optical device applications.

f) PLANS FOR THE FOLLOWING YEAR

This study will continue to explore the thermally stable NLO polymeric systems. Preliminary studies have shown that the molecular weight and polydispersities of the polymers affect the segmental relaxations and intermolecular cooperativity. We will continue to investigate how changing molecular level parameters affects relaxation behavior. The side-chain functionalized polyarylene ethers currently investigated do not show enhanced temporal stability following poling as compared to the guest-host systems. This may be because of the small NLO chromophores used. Larger chromophores and spacer units will be incorporated into these side-chain functionalized systems, and the influence of these changes on the relaxation behavior will be examined. Second harmonic generation and dielectric relaxation will be employed to examine the relaxation behavior. Second harmonic generation is sensitive to small degrees of chromophore rotational mobility and local changes in the polymer microenvironment, and thus is an excellent technique for studying effects of chromophore functionalization and polymer molecular weight on relaxations. Dielectric relaxation is a useful technique for studying transitions, relaxations, and intra- and intermolecular interactions in polymeric materials.

g) Graduate student funded: Ms. Stacey Fu (permanent resident).

Part III.
a. Introductory view-graph discussing research
b. Figure representing the highlight
c. Concluding view-graph
d. Paragraph of explanatory text

High temperature stable materials are necessary to produce polymers that are useful for second order NLO devices. Most of the recent research mainly focus on synthesizing polymers with high glass transition temperatures and rigid backbones that would minimize the randomization of chromophore orientation following poling, improving the optical stability. The studies of polymer physics of these high temperature stable polymeric materials are still incomplete. This research investigates the structure/property relationships that influence the segmental relaxations and intermolecular cooperativity of the thermally stable polyarylene ethers. Changes in the polymer backbone structure affected the intermolecular cooperativity and segmental relaxations. As shown in Figure 1, the dielectric loss curve became broader, particularly on the low-frequency side, as the pendant groups on the polymer backbone became more polar and/or more sterically hindered, indicating that the segmental relaxations were more intermolecularly coupled. The effect of chromophore functionalization on the relaxation behavior and intermolecular cooperativity was examined. As indicated in Figure 2, the dispersion curves were broader in the two side-chain functionalized systems, PP-PEPO-pNPH and PP-PEPO-DNPH, than the undoped PP-PEPO, indicating stronger intermolecular coupling between the covalently bonded chromophores and polymer. The effect of physical aging during poling on the chromophore orientational dynamics was also examined. Aging the material during poling allows the polymer matrix to densify around the oriented dopants, hindering them from rotating out of poling induced orientation after the applied voltage is turned off and thus improving the temporal stability of chromophore orientation. As shown in Figure 3, better temporal stability of dopant orientation for the 10 wt.% DANS doped PP-PEPO system aged at T_g - 140°C for 17 and 31 hours was indeed observed when compared to that of the unaged sample. It is critical to understand polymer physics and structure/property relationships governing the relaxation behavior in the NLO polymeric materials so that one can better tailor the materials for a particular device applications.

HIGH TEMPERATURE STABLE MATERIALS FOR SECOND ORDER NONLINEAR OPTICS AND PHOTONIC DEVICES

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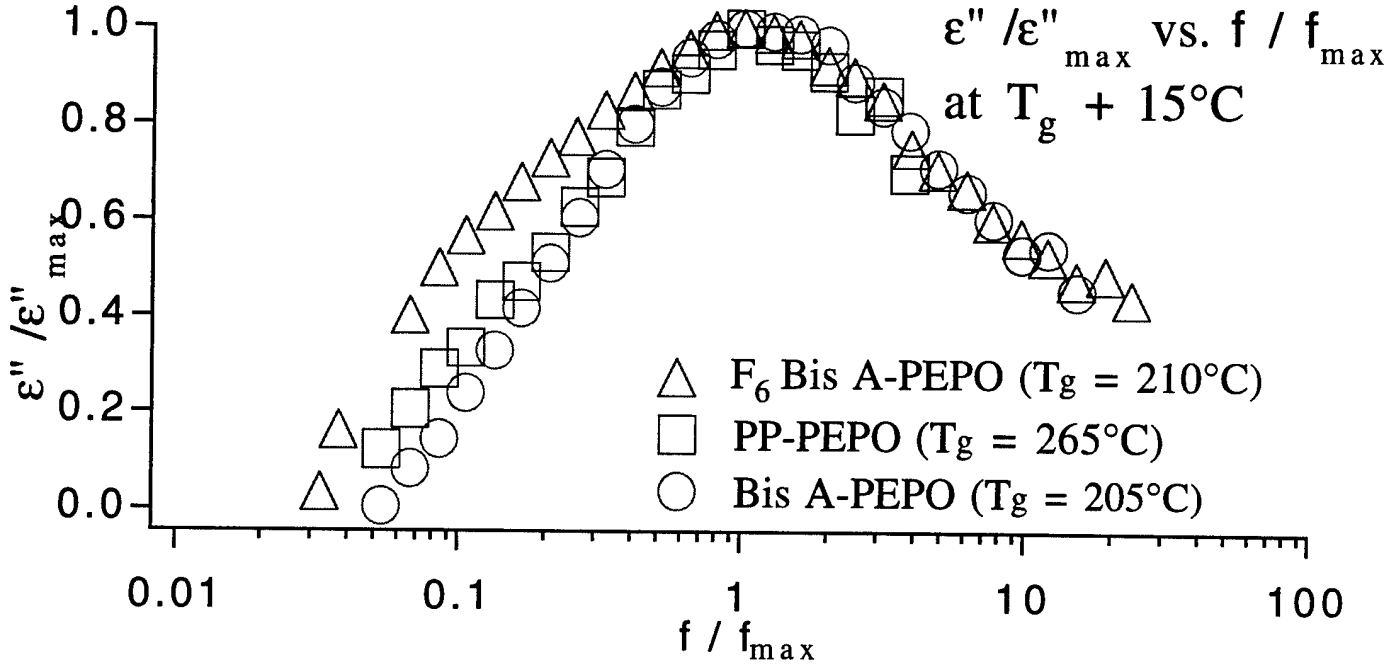
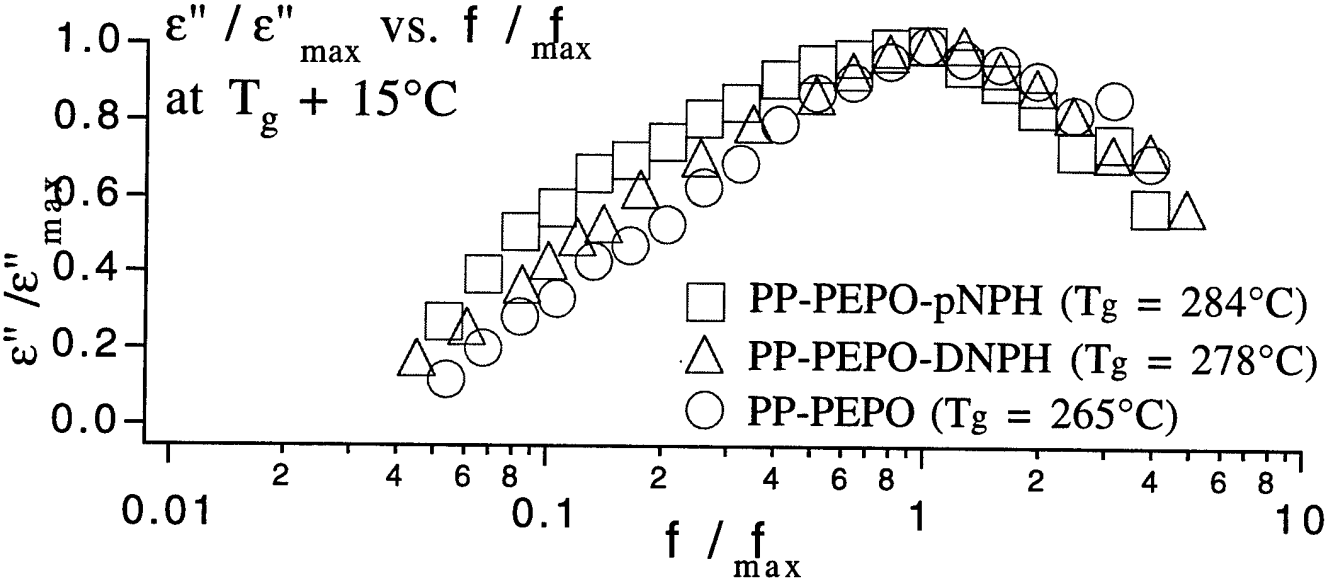
High temperature stable polymers generate second order nonlinear optical materials with enhanced thermal and temporal stability

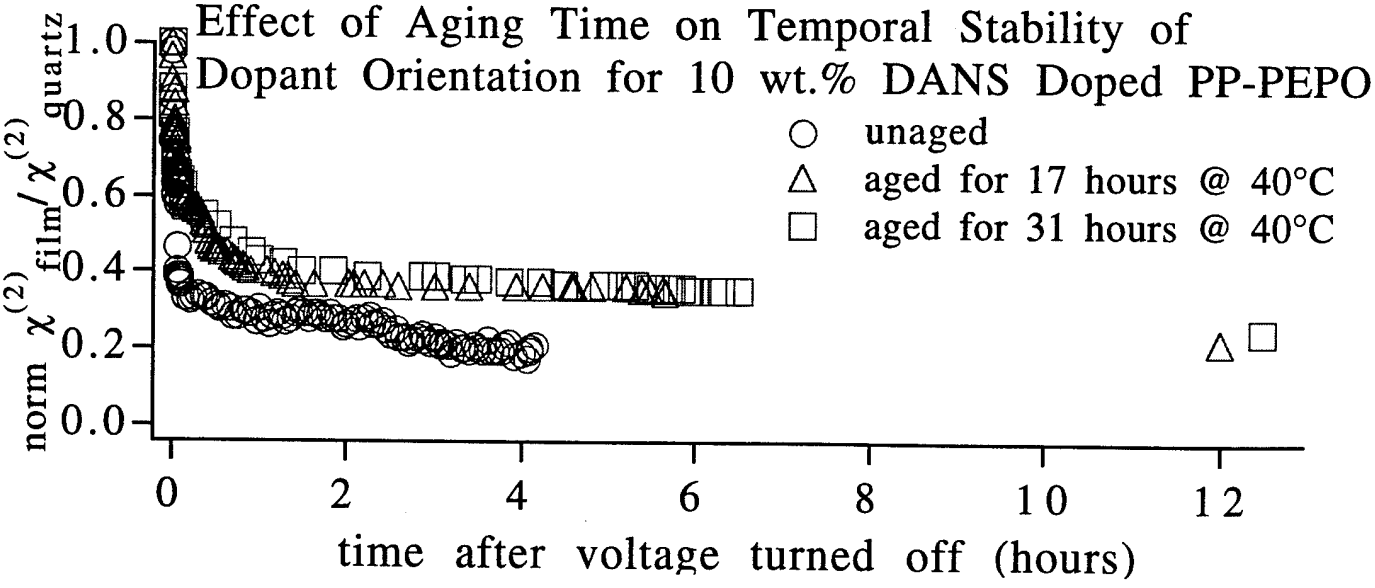
Systematic studies on how STRUCTURE/PROPERTY RELATIONSHIPS affect chromophore orientational dynamics and polymer relaxations in thermally stable polyarylene ethers allow improved tailoring of materials properties

- Technological Advantages of Polymers studied:
  - Stable to high temperatures (up to 350°C+)
    - high temporal stability of chromophore orientation
  - low index of refraction
  - low dielectric constant
  - low scattering, losses
  - good mechanical properties
  - Hydrogen bonding sites available to interact with chromophores

  - molecular "tunability"
  - easy to process
  - low cost
  - large NLO figure of merit


ε" /ε"max vs. f / fmax
at Tg + 15°C
ε" /ε"max
f / fmax
F6 Bis A-PEPO (Tg = 210°C)
PP-PEPO (Tg = 265°C)
Bis A-PEPO (Tg = 205°C)


ε" / ε"max vs. f / fmax
at Tg + 15°C
ε" /ε"max
f / fmax
PP-PEPO-pNPH (Tg = 284°C)
PP-PEPO-DNPH (Tg = 278°C)
PP-PEPO (Tg = 265°C)


Effect of Aging Time on Temporal Stability of
Dopant Orientation for 10 wt.% DANS Doped PP-PEPO
unaged
aged for 17 hours @ 40°C
aged for 31 hours @ 40°C
norm χ(2) film/χ(2) quartz
time after voltage turned off (hours)

Generate novel, use-specific polymeric photonic materials for military and commercial device applications.

•**Design** and **modify** the temporal/thermal stability of NLO-phore orientation and resultant optical stability by **understanding** and **manipulating** polymer processing.

•Study polymer dynamics and mobility at the submolecular level.

•**Understand the relationship between polymer physics and advanced materials design and performance.**

SPECIFIC ISSUES STUDIED:

- Understand structure/property relationships including **polymer backbone structures and molecular weight**, **chromophore/polymer interactions,** and **chromophore functionalization** influencing intermolecular cooperativity and segmental relaxation behavior of polymers.

- Investigate **effect of physical aging during poling on** temporal stability of chromophore orientation.

ADDITIONAL INFORMATION: SELECTED ABSTRACTS OF MANUSCRIPTS TO BE PUBLISHED WITH OFFICE OF NAVAL RESEARCH GRANTEES

(note: I have submitted copies of each manuscript published with funds from this grant. Below I enclose abstracts of manuscripts in press, or submitted for your information. Note that these are manuscripts in which I am the "major" contributor; Professor Wright will be submitting his own version of this section.)

Submitted to Chemistry of Materials:

Relaxations in Indole-Based Polymers and the Synthesis of Stabilized Polymer Blends and Main-Chain and Side-Chain Functionalized Polymers for Second Order Nonlinear Optics

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West Lafayette, Indiana 47907-1283

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Logan, Utah 84322-0300

Abstract

The potential of indole-based polymers as temporally and thermally stable, efficient secon order nonlinear optical (NLO) materials has been explored by examining the chromophor orientation as a function of processing. Several new indole-based NLO-phores/monomers wer synthesized. In order to enhance temporal stability following removal of the applied corona fiel polystyrene was blended into the reactive indole systems and thermal polymerization wa initiated *in-situ* during processing. By preparing samples with and without a reactive S catalyst, a comparison of structure/property relationships could be developed relating loc chemistry to bulk chromophore orientation dynamics and nonlinear optical response. Gues host, side-chain, and main-chain functionalized polymers and blends were synthesized an examined for second harmonic generation. The greatest temporal stability was observed for sid chain functionalized indole polymers blended with a polystyrene matrix. The effect chromophore size on orientational stability during processing was also investigated. Possibl mechanisms to describe the observed relative temporal stabilities as a function of structure ar discussed.

Submitted to Proc. SPIE:

Polymer Physics in Poled Polymers for Second-Order Nonlinear Optics

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ABSTRACT

A new class of high temperature stable polymers called poly(arylene ether) phosphine oxides is currently being investigated. These polymers are of interest for second-order nonlinear optical applications because of their high glass transition temperatures (>200°C). They also have strong hydrogen bonding sites that can interact with the chromophores. This work describes the polymer physics including structure/property relationships; in particular, the chromophore/polymer interactions and polymer backbone structures that influence the thermal and temporal stability of chromophore orientation in

these polymer matrices. Second harmonic generation is sensitive to local changes in the polymer microenvironment, and thus is an excellent technique for probing chromophore orientational dynamics during and following electric field poling and the effect of dopant/polymer interactions on the temporal stability. Dielectric relaxation is employed to examine the intermolecular cooperativity and segmental relaxation behavior arising from different polymer backbone structures and steric effects. It is critical to understand how structure/property relationships affect the chromophore orientational dynamics and polymer relaxation in these polymers so that one can better tailor the materials for nonlinear optical device applications.

Submitted to Macromolecules:

POLYMER PHYSICS AND STRUCTURE/PROPERTY RELATIONSHIPS OF THERMALLY STABLE POLYARYLENE ETHERS FOR SECOND ORDER NONLINEAR OPTICS

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ABSTRACT: This paper describes the structure/property relationships including the polymer backbone structures and molecular weight, chromophore/polymer interactions, and chromophore functionalization that influence the chromophore orientational dynamics and polymer relaxations in a special class of thermally stable polymers that was recently developed for second order nonlinear optical applications. These polyarylene ether polymers (synthesis and characterization reported elsewhere) are being investigated because of their high glass transition temperatures (>200°C), which may minimize the randomization of chromophore orientation following electric field poling. They also have hydrogen bonding sites that can interact with the chromophores, which may improve the temporal stability of chromophore orientation following poling. Second harmonic generation, a second order nonlinear optical effect, and dielectric relaxation are the two techniques employed to examine the intermolecular cooperativity and segmental relaxation behavior in these polymers. By examining the second order nonlinear optical properties of the doped or functionalized polymeric material as a function of time and temperature, and the dielectric relaxation phenomena as a function of frequency and temperature, information concerning the local mobility and relaxation phenomena of the polymer microenvironment surrounding the nonlinear optical chromophores can be obtained. The dielectric loss data were analyzed using the Havriliak-Negami empirical function and the Schonhals and Schlosser model to examine the extent of intermolecular coupling in these polymer systems. Results obtained using these two techniques are correlated.

Submitted to ACS Books <u>Dielectric Spectroscopy of Polymeric Materials</u>
James P. Runt and John J. Fitzgerald, Editors
C.Y. Stacey Fu, Mark H. Ostrowski, and Hilary S. Lackritz*
ABSTRACT

Dielectric relaxation and second harmonic generation, a second order nonlinear optical technique, can be used to study the rotational Brownian dynamics of the nonlinear optical chromophores doped or functionalized into a polymer matrix as a function of time/frequency and temperature. By combining these two techniques, one can determine

more quantitatively how the thermal and temporal stability of chromophore orientation relates to specific polymer motions. Furthermore, the relationships between the intra- and intermolecular cooperativity and polymer structures and properties can be better understood. This information is critical for designing novel nonlinear optical polymeric materials for optical device applications.

Study of Poling and Relaxation in Kink and Linear Main-Chain Functionalized Polymers for Second Order Nonlinear Optical Applications
Liu, L. Y.; Lackritz, H. S.; Wright, M. E.; Mullick, S. *Macromolecules* **1995**, *28*, 1912-1920.

ABSTRACT. The rotational dynamics of nonlinear optical chromophores functionalized to polymer main chains were studied using second harmonic generation. Corona poling was used to orient the chromophores into the bulk noncentrosymmetric structure required to observe second order nonlinearity. In order to detect different microscopic relaxation mechanisms of the polymers, chromophores were incorporated into the polymer main chain but positioned in two different ways. It was found that for a kink polymer, in which the chromophores were placed at an angle away from the major molecular axis of the polymer chain, the motion of the tilted chromophores may occur through local segmental motion. For a linear polymer, which had the same chromophore, but directed parallel to the chain direction, a large scale main-chain motion was involved in orientation. Therefore, the end-to-end vectors of the polymer chains could be detected. The temperature dependence of the second order nonlinearity in these polymers showed that there was an optimum temperature at which the main-chain chromophores could be relatively easily oriented during poling. The retarded polymer mobility at lower temperatures and the enhanced rotational Brownian motion at higher temperatures reduced the degree of the chromophore alignment and therefore a less second order signal was observed during poling. Dielectric relaxation spectroscopy showed that the bulk conductivity and crystallinity might also contribute to the decrease in second order nonlinearity observed at high temperatures.